MOLECULAR SIEVES BASED NANO-COMPOSITE UV-RESISTANT MATERIAL, PREPARATION PROCESS AND USE THEREOF

FIELD OF THE INVENTION

The present invention relates to the preparation of UV-resistant material, in particular, it relates to an UV-resistant material which is made with crystalline porous material such as zeolite molecular sieve and mesoporous molecular sieve being the host and the nano-cluster TiO_2, ZnO, CeO_2, and Fe_2O_3 being the guest, The present invention also relates to the preparation method and the use thereof.

BACKGROUND OF THE INVENTION

By reason of the development of modern industry, the atmospheric pollution is worsening and the damage level of ozonsphera is serious increasingly in recent years. It is an imminent problem to resist the ultraviolet radiation in quite a number of the fields. The hazard of excess UV is mainly incarnated in the following aspects:

1: The peptide chain of the protein will be damaged when uv irradiate on the organism, which result in the produce of free radicles. The free radicles will further act with other peptide chains and eventually result in tissue damage and gene mutation. For a human body, it will result in skin burn injury and the produce of skin cancer. Using sun-prevent cosmetics is one of the efficient ways to resolve the above problems.

2: The ultravioletlight is high energy ray which will lead to molecule industrial product aging and lifeshortening. Therefore in general high molecule products will be added with UV-resistant agent.

In some countries, such as the United States, Japan and Europe, the research and the use of sun-prevent cosmetic have reached a high level sun-prevent cosmetics have become a key point of the developing of cosmetic for skincare. The annual growth rate of sun-prevent cosmetics is 5-10% in Europe. It has been

reported that the yield of sun-prevent cosmetics accounted for a half of the inventory of the cosmetics in 1990 in the United States. In our country, with the rapid progress of the living standard, enhancement of people's consciousness of aesthetics and health care, many people are paying more attention to UV proofing. The increasing rate of sun-prevent product market in our countries is kept above 20% from the 1990s metaphase. Moreover, UV-resistant agent is also more and more used. In plastic material, rubber and paint industry, especially In paint industry, highly active and steady UV-resistant agents have always been a key point of R&D.

The developed UV-resistant materials include two main classes of chemical and physical at present. The use of the former is more popular. The chemical UV-resistant agents in general are organic compounds, therefore they have good compatible but they also generally have certain toxicity and irritancy to the skin. They are not consistent with the healthy current of people at the present, because it is easy to cause anaphylaxis when they are used in the products which contact with the skin directly. In addition, the organo-UV-resistant agents always have bad photostability and they will be decompounded or oxidised under uviolize. The development of nanometer techniques allows solutions for resolving above problems. They are physical UV-resistant agents developed with nanometer techniques, i.e. the abio-nanometer UV-resistant agents. Abio-nanometer UV-resistant agents have characteristics of stabilization and broad-spectrum, they make up the disadvantages of the organo-UV-resistant agents to a certain degree. With the application, the shortcomings of abio-Nanometer UV-resistant agents have come out increasingly. The surface activity is most typically. By reason of the high surface energy of the abio-Nanometer particles, when they are mixed with the organic phase, it is easy to occur coacervation and resulting in the inactivating of the UV-resistant agents.Together, the security is also the potential problems of the application of the nanometer particles.

For instance, nano-ZnO and nano-TiO_2 have photocatalysis reactiveness and

will produce free radicles under daylight, it will do harm to DNA of human body. John Kownland etal. of Oxford have researched the negative effect of and ZnO deeply. It is stated that TiO_2 and ZnO produce oxygen and oxyhydrogen free radicles in photoillumination. Different from the knowledge of the people, it is proved that it is oxyhydrogen free radicles do harm to DNA of the human body, while oxygen radicals do not. Therefore, the method of adding oxygen radical scavenging agent to proof the harm of TiO_2 and ZnO is not enough. The nano-cluster assembling with molecular sieve being the host can resolve the above problem drastically.

Molecular sieve is a kind of crystalline and porous material. Its porous channel has characteristic of narrow distribution of pore size and high-ordered in microcosmic. Using the porous channel of molecular sieve as a template, assembling the guest molecule into the porous channel, high ordered nano-cluster arrangement can be obtained. The assembling technique can not only ensure the disperseion of the nano-cluster, but also enhance the performance of the nano-cluster to a large extent. Many assembling methods have been developed in this field. In researching the assembling methods of semiconductor-guest, coordination compound-guest and some macromolecule organo-guest, a kind of technique known as "ship in bottom" has been developed.In short, this method is to introduce the guest monomer micromolecule into the porous channel of the molecular sieve, then initiate the condition of synthetic reaction in porous channel to occur the combination reaction.To use synthetic method in situ sometimes has goodish effect when assembling some nitrogencontaining based organo-guest.The composite materials obtained from the above method behave as macro granulometric pattern professedly yet have nano-cluster characteristics virtually.Furthermore, By reason of the template action of the porous channel of the molecular sieve, the guest behave as ordered microcosmic height. It let the material properties occur changes of order of magnitude to a large extent.

This type of assembling methods appears high application merit in

sun-prevent cosmetics, coatings, rubber and plastics industry. Whether the conventional organo-ultraviolet absorption material, or the new style abio - ultraviolet absorption material, they can place the technical group into the porous channel of the molecular sieve to avoid the coacervation of nanometer particles, and this technical solution can also farthest reduce the side-effect of the ultraviolet absorption agent. It is more important that the performance of ultraviolet absorption can be enhanced extremely by reason of the high ordered microcosmic state of the ultraviolet absorption agent.

One object of the present invention is to provide a kind of UV-resistant material.

Another object of the present invention is to provide the method of preparation of said UV-resistant material.

Another object of the present invention is to provide the use of said UV-resistant material.

The description of the invention

The present invention provides a UV-resistant material which use molecular sieve based host-guest nano-composite materials as the ultraviolet absorption agent. The host is selected from one or more than one material of micro- and mesoporous molecular sieves types, such as X, Y, A, STI, ZSM-5, MCM-41 and the series thereof, and SBA and the series thereof, the guest-cluster is selected from one or more than one material of $Ti0_2$, ZnO, $Ce0_2$, and Fe_20_3. This kind Of UV-resistant material use the microcosmic ordered porous channel of the molecular sieve as a template. The guest-cluster is directionally with high-order by the quantum confinement effect. The nano-cluster can be ensured that only the interval plane of the nano-clusters exist steadily, but also the performance is improved greatly.

The present invention also provides two preparation methods of the UV-resistant material.

The first preparation method uses any one or more than one material of $TiCl_3$, $Ti(NO_3)_3$, $ZnCl_2$, $Zn(NO_3)_2$, CeCl, $Ce(NO_3)_3$, $FeCl_3$, $Fe(NO_3)_3$, $FeSO_4$ as the

initiating material to synthesize the host-guest nano-composite materials by means of ion exchange, which are TiO_2, ZnO, CeO_2, Fe_2O_3 metal oxide nano-cluster and the molecular sieve compound, the product is used as the ultraviolet absorption agent to obtain the UV-resistant material.

This method include following steps: dissolving the initiating material in the water, adding the molecular sieve, stirring at room temeperature for 3-12 hours, filtrating, washing, torrefying at 400-600℃ for 4-24 hours.

Alternatively, dissolving the initiating material in the water, adding low-silicon molecular sieve, resting for 1 hours, filtrating, washing and drying at 80℃, torrefying for at 500℃12 hours.

The second preparation method use butyl titanate as the initiating material to synthesize host-guest nano-composite materials of TiO_2 cluster within mlecular sieve compound by means of hydrolytic reaction, the product is used as the ultraviolet absorption agent to obtain the UV-resistant material.

This method include following steps: mixing butyl titanate with high-silicon molecular sieve in non-polar solvent, with inert gas shielding, refluxing and agitating at 50-100℃ for 4-48 hours, washing the product by alcohol type solvent, drying at 60-100℃, torrefying for 4-24 hours at 400-600℃.

The Present invention further provides the use of the UV-resistant material In cosmetics ,coatings ,Rubber and plastics industry.

Embodiment

The present invention will be further expatiated with the following examples, but the invention is not to be limited to the examples given herein.

Example 1

Assembling of X zeolite and ZnO.

1) Weighing out 10.00g of $Zn(NO_3)_2$ and dissolving it in 40 ml deionized water;

2) Weighing out 2.00g of X zeolite, mixing with the above solution, maintaining

the PH equal to 4～5;

3) Electromagnetic stirring for 1 hours at 40～50℃;

4) Resting a moment, pouring discarding the supernatant liquor after delamination, weighing out 10.00g of $Zn(NO_3)_2$, dissolving it in 40ml water, electromagnetic stirring for 1 hours;

Repeating the step 4 for three times, filtrating the solution by buchner funnel in the last time, repetitive washing by deionized water to remove the impurity ion in the solution and Zn^{2+} out of the framework of the zeolite molecular sieve, then placing it in an oven, drying for about 30 minutes at 60℃;

6) Triturating the obtained product in an agate mortar for 10～15 minutes, then placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

7) Taking out the firepot, triturating the powder form for 10～15 minutes, replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product H-X-ZnO powder form.

Example 2

Assembling of Y zeolite and ZnO.

1) Weighing out 10.00g of $Zn(NO_3)_2$ and dissolving it in 40 ml deionized water;

2) Weighing out 2.00g of Y zeolite, mixing with the above solution, maintaining the PH equal to 4～5;

3) Electromagnetic stirring for 1 hours at 40～50℃;

4) Resting a moment, discarding the supernatant liquor after delamination, weighing out 10.00g of $Zn(NO_3)_2$, dissolving it in 40ml water, electromagnetic stirring for 1 hours;

Repeating the step 4 for three times, filtrating the solution by buchner funnel in the last time, repetitive scrubbing by deionized water to remove the impurity ion in the solution and Zn^{2+} out of the framework of the zeolite molecular sieve, then placing it inan oven, drying for about 30 minutes at 60℃;

6) Triturating the obtained product in an agate mortar for 10～15 minutes, then

placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

Taking out the firepot, triturating the powder form for 10～15 minutes, replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product H-Y-ZnO powder form.

Example 3

Assembling of A zeolite and ZnO.

1) Weighing out 10.00g of $Zn(NO_3)_2$ and dissolving it in 40 ml deionized water;

2)Weighing out of 2.00g zeolite, mixing with the above solution, maintaining the PH equal to 4～5;

3) Electromagnetic stirring for 1 hours at 40～50℃;

4)Resting a moment, discarding the supernatant liquor after delamination, weighing out 10.00g of $Zn(NO_3)_2$, dissolving it in 40ml water, electromagnetic stirring for 1 hours;

Repeating the step 4 for three times, filtrating the solution by buchner funnel in the last time, repetitive washing by deionized water to remove the impurity ion in the solution and Zn^{2+} out of the framework of the zeolite molecular sieve, then placing it in an oven, drying for about 30 minutes at 60℃;

6) Triturating the obtained product in an agate mortar for 10～15 minutes, then placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

Taking out the firepot, triturating the powder form for 10～15 minutes, replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product H-A-ZnO powder form.

Example 4

Assembling of STI zeolite and ZnO.

1) Weighing out 10.00g of $Zn(NO_3)_2$ and dissolving it in 40 ml deionized water;

2) Weighing out 2.00g of STI zeolite, mixing with the above solution, maintaining the PH equal to 4～5;

3) Electromagnetic stirring for 1 hours at 40～50℃;

4) Resting a moment, discarding the supernatant liquor after delamintion, weighing out 10.00g of $Zn(NO_3)_2$, dissolving it in 40ml water, electromagnetic stirring for 1 hours;

Repeating the step 4 for three times, filtrating the solution by buchner funnel in the last time, repetitive washing by deionized water to remove the impurity ion in the solution and Zn^{2+} out of the framework of the zeolite molecular sieve, then placing it in the heatingoven, drying for about 30 minutes at 60℃;

6) Triturating the obtained product in an agate mortar for 10～15 minutes, then placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

Taking out the firepot, triturating the powder form for 10～15 minutes, replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product H-STI-ZnO powder form.

Example 5

Assembling of ZSM-5 zeolite and ZnO.

1) Weighing out 10.00g of $Zn(NO_3)_2$ and dissolving it in 40 ml deionized water;

2) Weighing out 2.00g of ZSM-5 zeolite, mixing with the above solution, maintaining the PH equal to 4～5;

3) Electromagnetic stirring for 1 hours at 40～50℃;

4) Resting a moment, discarding the supernatant liquor after delamination, weighing out 10.00g of $Zn(NO_3)_2$, dissolving it in 40ml water, electromagnetic stirring for 1 hours;

Repeating the step 4 for three times, filtrating the solution by buchner funnel in the last time, repetitive washing by deionized water to remove the impurity ion in the solution and Zn^{2+} out of frameword of the zeolite molecular sieve, then placing it inan oven, drying for about 30 minutes at 60℃;

6) Triturating the obtained product in an agate mortar for 10～15 minutes, then placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

Taking out the firepot, triturating the powder form for 10～15 minutes, replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product ZSM-5-ZnO powder form.

Example 6

Assembling of MCM-41 zeolite and ZnO.

1) Weighing out 10.00g of $Zn(NO_3)_2$ and dissolving it in 40 ml deionized water;

2) Weighing out 2.00g of MCM-41 zeolite, mixing with the above solution, maintaining the PH equal to 4～5;

3)Electromagnetic stirring for 1 hours at 40～50℃;

4) Resting a moment, discarding the supernatant liquor after delamination, weighing out 10.00g of $Zn(NO_3)_2$, dissolving it in 40ml water, electromagnetic stirring for 1 hours;

5) Repeating the step 4 for three times, filtrating the solution by buchner funnel in the last time, repetitive washing by deionized water to remove the impurity ion in the solution and Zn^{2+} out of the framework of the zeolite molecular sieve, then placing it in the heatingoven, drying for about 30 minutes at 60℃;

6) Triturating the obtained product in an agate mortar for 10～15 minutes, then placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

7) Taking out the firepot, triturating the powder form for 10～15 minutes, replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product H-MCM-ZnO powder form.

Example 7

Assembling of X zeolite and Fe_2O_3.

1) Weighing out 10.00g of $FeSO_4$and dissolving it in 40 ml deionized water;

2) Weighing out 2.00g of X zeolite, mixing with the above solution, maintaining the PH equal to 4～5;

3) Electromagnetic stirring for 1 hours at 40～50℃;

4) Resting a moment, discarding the supernatant liquor after delamination, weighing out 10.00g of $FeSO_4$, dissolving it in 40ml water, electromagnetic stirring for 1 hours;

5) Repeating the step 4 for three times, filtrating the solution by buchner funnel in the last time, repetitive washing by deionized water to remove the impurity ion in the solution and Fe^{2+} out of the framework of the zeolite molecular sieve, then placing it inan oven, drying for about 30 minutes at 60℃;

6) Triturating the obtained product in an agate mortar for 10～15 minutes, then placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

7) Taking out the firepot, triturating the powder form for 10～15 minutes, replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product H-X-Fe_2O_3 powder form.

Example 8

Assembling of Y zeolite and Fe_2O_3.

1) Weighing out 10.00g of $FeSO_4$ and dissolving it in 40 ml deionized water;

2) Weighing out 2.00g of Y zeolite, mixing with the above solution, maintaining the PH equal to 4～5;

3) Electromagnetic stirring for 1 hours at 40～50℃;

4) Resting a moment, discarding the supernatant liquor after lamintion, weighing out 10.00g of $FeSO_4$, dissolving it in 40ml water, electromagnetic stirring for 1 hours;

5) Repeating the step 4 for three times, filtrating the solution by buchner funnel in the last time, repetitive washing by deionized water to remove the impurity ion in the solution, then placing it in an oven, drying for about 30 minutes at 60℃;

6) Triturating the obtained product in an agate mortar for 10～15 minutes, then placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

7) Taking out the firepot, triturating the powder form for 10～15 minutes,

replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product H-Y-Fe_2O_3 powder form.

Example 9

Assembling of A zeolite and Fe_2O_3.

1) Weighing out 10.00g of $FeSO_4$ and dissolving it in 40 ml deionized water;

2) Weighing out 2.00g of A zeolite, mixing with the above solution, maintaining the PH equal to 4～5;

3) Electromagnetic stirring for 1 hours at 40～50℃;

4) Resting a moment, discarding the supernatant liquor after lamintion, weighing out 10.00g of $FeSO_4$, dissolving it in 40ml water, electromagnetic stirring for 1 hours;

Repeating the step 4 for three times, filtrating the solution by buchner funnel in the last time, repetitive washing by deionized water to remove the impurity ion in the solution, then placing it in an oven, drying for about 30 minutes at 60℃;

6) Triturating the obtained product in an agate mortar for 10～15 minutes, then placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

7) Taking out the firepot, triturating the powder form for 10～15 minutes, replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product H-A-Fe_2O_3 powder form.

Example 10

Assembling of STI zeolite and Fe_2O_3.

1) Weighing out 10.00g of $FeSO_4$and dissolving it in 40 ml deionized water;

2) Weighing out 2.00g of STI zeolite, mixing with the above solution, maintaining the PH equal to 4～5;

3) Electromagnetic stirring for 1 hours at 40～50℃;

4) Resting a moment, discarding the supernatant liquor after lamintion, weighing out 10.00g of $FeSO_4$ again, dissolving it in 40ml water, electromagnetic

stirring for 1 hours;

5) Repeating the step 4 for three times, filtrating the solution by buchner funnel in the last time, repetitive washing by deionized water to remove the impurity ion in the solution, then placing it in an oven, drying for about 30 minutes at 60℃;

6)Triturating the obtained product in an agate mortar for 10～15 minutes, then placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

Taking out the firepot, triturating the powder form for 10～15 minutes, replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product H-STI-Fe_2O_3 powder form.

Example 11

Assembling of MCM-41 zeolite and Fe_2O_3.

1) Weighing out 10.00g of $FeSO_4$ and dissolving it in 40 ml deionized water;

2) Weighing out 2.00g of MCM-41 zeolite, mixing with the above solution, maintaining the PH equal to 4～5;

3) Electromagnetic stirring for 1 hours at 40～50℃;

4) Resting a moment, discarding the supernatant liquor after lamintion, weighing out 10.00g of $FeSO_4$, dissolving it in 40ml water, electromagnetic stirring for 1 hours;

5) Repeating the step 4 for three times, filtrating the solution by buchner funnel in the last time, repetitive washing by deionized water to remove the impurity ion in the solution, then placing it in an oven, drying for about 30 minutes at 60℃;

6) Triturating the obtained product in an agate mortar for 10～15 minutes, then placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

7) Taking out the firepot, triturating the powder form for 10～15 minutes, replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product H-MCM-Fe_2O_3 powder form.

Example 12

Assembling of CeO_2 nano-cluster in X, Y, A, ZSM-5, STI, and MCM-41 zeolite.

1) Weighing out 10.00g of $Ce(NO_3)_2$and dissolving it in 40 ml deionized water;

2) Weighing out 2.00g of zeolite (any one of X, Y, A, ZSM-5, STI, and MCM-41), mixing with the above solution, maintaining the PH equal to 4～5;

3) Electromagnetic stirring for 1 hours at 40～50℃;

4)Resting a moment, djiscarding the supernatant liquor after delamination, weighing out 10.00g of $Ce(NO_3)_2$, dissolving it in 40ml water, electromagnetic stirring for 1 hours;

5) Repeating the step 4 for three times, filtrating the solution by buchner funnel in last time, repetitive washing by deionized water to remove the impurity ion in the solution, then placing it in an oven, drying for about 30 minutes at 60℃;

6) Triturating the obtained product in an agate mortar for 10～15 minutes, then placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

7) Taking out the firepot, triturating the powder form for 10～15 minutes, replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product.

Example 13

Assembling of TiO_2 nano-cluster in X, Y, A, ZSM-5, STI, and MCM-41 zeolite.

1) Weighing out 10.00g of $TiCl_3$ and dissolving it in 40 ml deionized water;

2) Weighing out 2.00g of zeolite (any one of X, Y, A, ZSM-5, STI, and MCM-41), mixing with the above solution, maintaining the PH equal to 4～5;

3) Resting for 1 hours at room temperature;

4)Filtrating, repetitive washing by deionized water to remove the impurity ion in the solution, then placing it in an oven, drying for about 30 minutes at 60℃;

5)Triturating the obtained product in an agate mortar for 10～15 minutes, then placing it in a 30ml firepot, torrefying for 6 hours by muffle furnace at 550℃;

Taking out the firepot, triturating the powder form for 10～15 minutes, replacing it into the muffle furnace, torrefying for 6 hours under the same condition to obtain the product.

Example 14

The preparation of acrylic acid-azyl varnish:

	wt%
Acrylic resin （70% solid content ）	52.2
amino resin （70% solid content）	22.3
Tinnvin 292	0.5
Tinnvin 1130	0.8
drainning silicea （10%）	5.0
butyl acetate	5.0
dimethylbenzene	10.0
ethylene glycol monobutyl ether acetate	2.7
n-butyl alcohol	1.5

Synthetic method

1 Weighing mainly resin such as acrylic resin and amino resin precisely, placing them into clean and separated vessels;

2 First, adding high boiling point solvent such as butyl acetate and ethylene glycol butyl ether acetate into resin to make it be disluted, gradually increase the stirring rate;

3 Weighing out required Tinuvin 272 precisely, disluting it by a few butyl acetate or dimethylbenzene to make it be dispersed;

4 Weighing out different kinds of auxiliary agents such as drainning silica and diluting them by the same method and then adding them into the vessel;

5 Adding the left solvents into the vessel, dispersing under high speed (2000～3000rpm) for 20～30mins.

Example 15

The preparation of the sun block:

	wt%
A: refining water	50
polyoxyalkylene	12
polyacrylic acid solution	2
sodium lauryl sulfate	0.5
caisson	0.1
B: isopropyl myristate	10
isopropyl palmitate	10
acetylated lanolin	5
t-butyl hydroxyl anisole	0.05
C: nano-composite UV-resistant agent	8
mica powder	1
D. fragrance essence	0.85

Synthetic method:

Mixing and stirring A, B respectively to make them be resolved, emulsificating A, B, C, then adding E into the former, resting for 24 hours .